US Army Research Laboratory

Theoretical Prediction of the Heat of Formation, Density, and Relative Sensitivity for 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4] triazin-4-amine

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14. ABSTRACT

Using a series of scripts developed by the US Army Research Laboratory, written to dramatically simplify the computation of crystalline density and heat of formation, the performance properties for the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine notional energetic material were evaluated. Additionally, a qualitative estimation of the impact sensitivity has been calculated. This report outlines the procedures used to generate this information, as well as Cheetah calculations using the predicted crystalline density and heat of formation.

15. SUBJECT TERMS

computational toolbox, script, crystalline density, heat of formation, impact sensitivity, synthesis, energetic materials, 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine

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1.   Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation[1,2] and densities[3,4] of energetic materials. This capability, coupled with a growing ARL synthetic experimental faculty, allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. This technical note will detail theoretical predictions of a notional energetic material.

The tools are based on correlations of quantum mechanically derived properties of isolated energetic molecules with heats of formation and crystalline densities, critical elements in predicting the detonation and propulsion properties, for both neutral and ionic solid energetic materials. As the crystal structure of a novel material is usually unknown, as it has yet to be synthesized, each of the correlations requires quantum mechanical data solely from single molecules and not from knowledge of the bulk material. To date, the neutral heat of formation tool can only treat molecules containing carbon, hydrogen, nitrogen, and oxygen. Additionally, a tool to qualitatively predict the impact sensitivity for neutral molecules was developed, also based solely on quantum mechanically derived data based on a single molecule. This report details the theoretically predicted performance and vulnerability properties for notional energetic molecules; as such, we will recap the methodologies used in the predictions in this technical report.

1.1 Neutral Heat of Formation

Developed in 2006,[1] the neutral heat of formation prediction tool is based on Hess's law (Eq. 1),[5] where an atomic or group equivalency prediction for the gas phase heat of formation (Eq. 2) is added to a prediction for the heats of vaporization (Eq. 3) or sublimation (Eq. 4). Equations 2–4 use information determined from quantum mechanical calculations.

$$\Delta H^{\circ}_{f\,(liquid/sold)} = \Delta H^{\circ}_{f\,(g)} - \Delta H_{vap/sub}. \tag{1}$$

$$\Delta H^{\circ}_{f\,(g)} = E - \Sigma\ n_j\varepsilon_j. \tag{2}$$

$$\Delta H_{vap} = a(SA)^{\frac{1}{2}} + b(\sigma^2_{tot}v)^{\frac{1}{2}} + c. \tag{3}$$

$$\Delta H_{sub} = a(SA)^2 + b(\sigma^2_{tot}v)^{\frac{1}{2}} + c. \tag{4}$$

In Eq. 2, E is the quantum mechanically determined electronic energy, n_j is either the number of atom or group types j contained in the neutral molecule, and ε_j is

either the atom or group equivalent energy of atom/group j. These equivalent energies were determined through the fitting of experiment gas phase heats of formation [$\Delta H°_{f\,(g)}$] to quantum mechanically computed energies E.

Equations 3 and 4 use statistics derived from the electrostatic surface potential (ESP), as demonstrated by Politzer et al.[6–8], to correlate to heats of vaporization and sublimation. As defined in the Murray et al.[9] and Rice and Hare[10] papers, the definitions of these electrostatic properties are global properties across the 0.001 electron/bohr^3 isosurface of electronic density, an isosurface calculated to contain 98%–99% of the electronic density. To compute these statistics, the electrostatic potential V is required and is defined as

$$V(\mathbf{r}) = \sum_{i} \frac{Z_i}{|\mathbf{R}_i - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\mathrm{d}\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \,, \tag{5}$$

where Z_i and $\mathbf{R}_i$ represent the charge and position of atom i, and $\rho(\mathbf{r})$ is the electronic density. The statistical tools developed by Murray et al.[9,11] used in Eqs. 3 and 4 are the surface area (SA), the variance of electrostatic surface potential (σ^2), and the balance parameter (ν). These are defined as

$$\Sigma^x = \frac{1}{n} \sum_{i=1}^{n} V^x(r_i) \,, \tag{6}$$

$$\sigma_x^2 = \frac{1}{n} \sum_{i=1}^{n} |V^x(r_i) - \Sigma^x|^2 \,, \tag{7}$$

$$\sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 \,, \tag{8}$$

and

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{tot}^2]^2} \,, \tag{9}$$

where $V(r_i)$ is the value of the ESP at r_i and Σ is the average electrostatic surface potential (x is either the positive [+] or negative [–] portion of the ESP). SA is the surface area of the 0.001 electron/bohr^3 isosurface of the electron density of the molecule, σ^2_{tot} is a measure of the variability of electronic potential on the surface, and ν is the degree of balance between the positive and negative charges on the isosurface. Equations 3 and 4 contain a different set of fitted a, b, and c parameters. This methodology enjoys considerable accuracy, with the root mean square errors for the solid phase heat of formation under 6 kcal/mol.

1.2 Crystalline Density

Initially developed in 2007[3] and revised in 2013,[4] this method correlates the quantum mechanically derived electronic density volume of the molecular unit to the crystalline density. This correlation exhibits significant success in predicting the crystal density, with errors under 3% for neutral materials. This correlation only requires the quantum mechanically derived molecular volume and the molecular mass for a single molecular unit, along with associated electrostatic properties (Eq. 10).

$$\rho_{crystal} = a(\boldsymbol{M} / \boldsymbol{V_M}) + b(\nu\sigma^2_{tot}) + c, \tag{10}$$

where a, b, and c are fitted terms, different from those in Eqs. 3 or 4, $\boldsymbol{M}$ is the total molecular mass, $\boldsymbol{V_M}$ is the total molecular volume, and σ^2_{tot} and ν are the same as in Eqs. 8 and 9.

1.3 Impact Sensitivity

Besides performance parameters, ARL researchers have also developed a visual qualitative indicator of impact sensitivity (David Chavez, Los Alamos National Laboratory, private communication, 2014; unreferenced) as a method to assess any potential safety concerns with yet to be synthesized novel materials. Rice and Hare[12] attempted to correlate Politzer-type statistical properties of the electronic density to impact sensitivity for a series of polynitroaromatic and benzofuroxan molecules. While no strong correlations were found with the statistical parameters, there was a qualitative visual correlation related to the degree of electron deficiency over covalent bonds contained within the "backbone" of the molecules. Molecules that were very sensitive exhibited large electron deficiencies over the main structure, while less-sensitive molecules had a more evenly distributed electron density. This method, while quite approximate and limited to neutral molecules (due to the inherent charge separation found in ionic materials), can still yield a relative means of estimating impact sensitivities and thus potential hazards of notional materials. The visualizer used in this study, titled EDAT, was originally coded by Dr Jennifer Hare and later revised by Dr Anthony Yau. This tool is also used to derive the Politzer statistical properties used in the heat of formation and density predictors. In this report we shall apply these methods toward the molecule 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (David Chavez, Los Alamos National Laboratory, private communication, 2014; unreferenced) to predict the heat of formation and crystalline density of this material.

2. Method of Solution

The analysis was performed using scripts written at ARL to perform the following required computations[12]:

1. A driver script that calls the other scripts, as well as submits the required Gaussian09[13] calculations and monitors the queues (master_densheat.s.)

2. A script to construct the Gaussian input files (gbuild.s).

3. A script to gather and compute the data needed to determine the heats of formation and/or crystalline densities and subsequently calculate said properties (arl_densheat.s).

Given a properly formatted input file, the scripts will analyze the .dat input file, design the proper Gaussian input files and submit them, monitor the supercomputer queues for job completion, postprocess the necessary files, and, finally, compute the desired information.

The scripts also perform a limited series of error checking, such as checking that structures are optimized (i.e., the structure is not a transition state structure but rather a minimum), that the Gaussian calculations ran successfully to completion, and that, for neutral calculations, the number of atom types listed correspond to the number of atoms in the Cartesian coordinates.

The initial, user-designed structure has its geometry optimized using the B3LYP spin-restricted Kohn-Sham density functional theory (KS-DFT)[14] with the 6-31G* Pople Gaussian basis set,[15] currently done using the Gaussian09 program package.[13] For the computation of the electronic energy required in Eq. 2, the B3LYP density functional theory energy[15] with the 6-311++G(2df,2p) Pople basis set[16] is obtained on the optimized geometry. For the crystalline density, the initial structure is optimized using the B3LYP KS-DFT with the 6-31G** Pople basis set,[16] with the associated electronic density used in obtaining the molecular volume and electronic statistical properties required in Eq. 10. The visualization of the electrostatic potential surface was performed with the EDAT tool.

3. Results and Discussion

The 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule (David Chavez, Los Alamos National Laboratory, private communication, 2014; unreferenced) (Fig. 1) was constucted and submitted with the ARL scripts.[12]
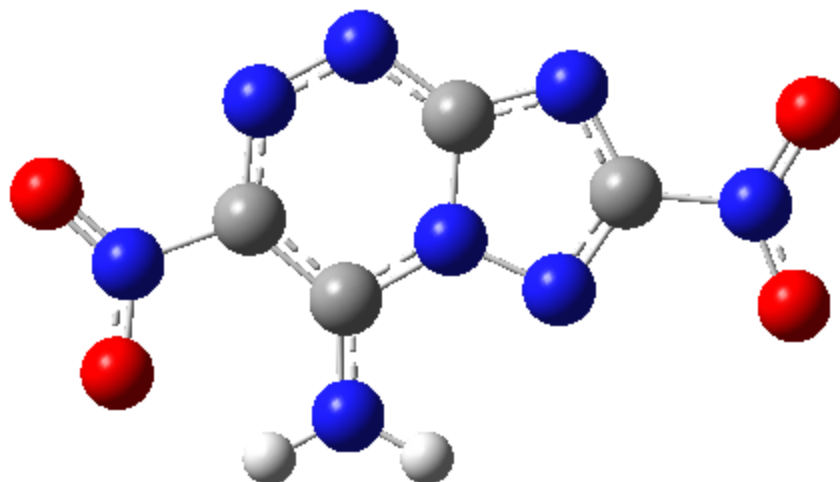
Fig. 1   Optimized structure of the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule

The resultant crystal density was computed to be 1.856 g/cc. The gas and solid phase heats of formation from the group additivity methodology were 120.12 and 95.22 kcal/mol, respectively.

Using the ARL-developed EDAT tool, the electrostatic map on the 0.001 isosurface was generated and is illustrated in Figs. 2 and 3 (with and without the molecule overlaid). For this visualization, the scalar range of the ESP ranges from –0.05 to 0.075. For this visualization methodology, regions of large positive charge (red) over the backbone of the structure tend to indicate increased sensitivity. For this molecule, this ESP distribution would indicate moderate impact sensitivity. Using this predicted data, we then performed Cheetah 7.0 calculations[18] to predict the performance parameters (Table).
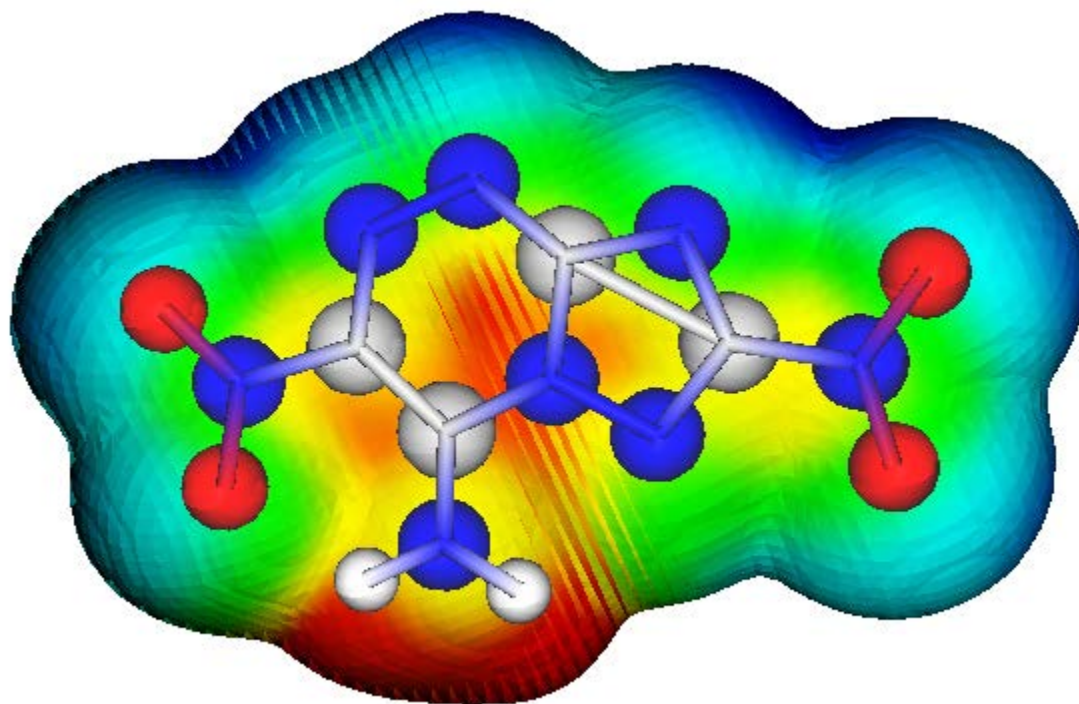
Fig. 2 Electrostatic potential map of the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule, with molecule overlay
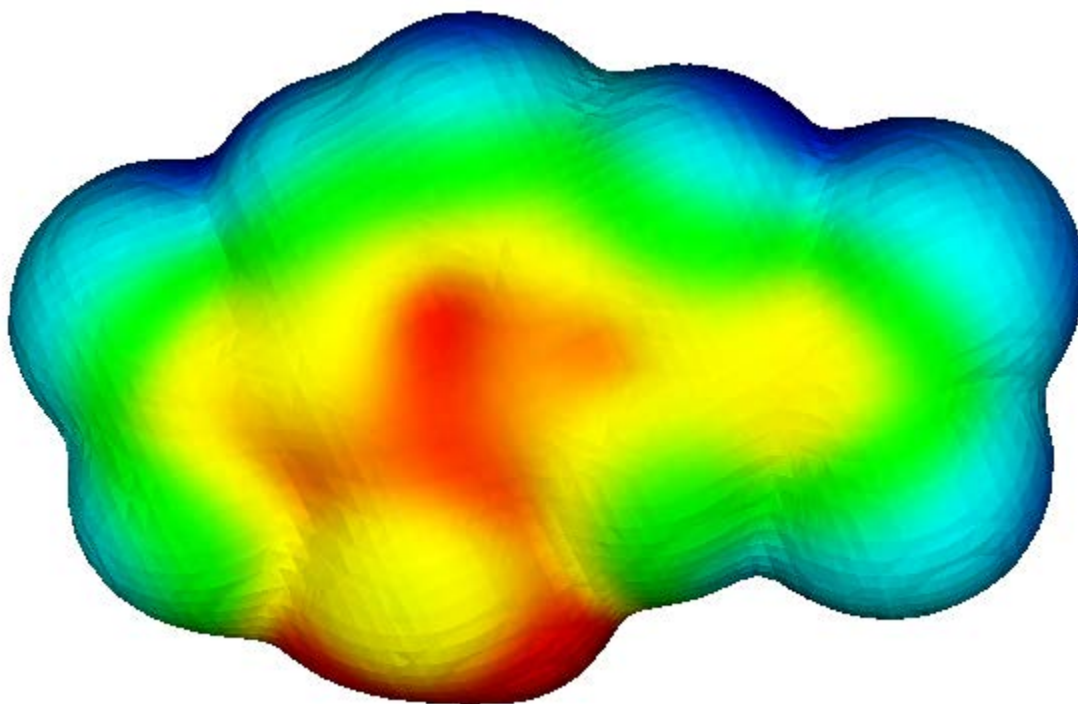

Fig. 3 Electrostatic potential map of the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule, without molecule overlay

Table   Cheetah-predicted properties of the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule

Property	Value
Pressure	31.084 GPa
Shock velocity	8.679 km/s
Temperature	3,395.8 K
Total energy of detonation	1.284 TNT equivalence (per cc)
	1.145 TNT equivalence (per gram)

4.   Conclusions

The ARL-developed software tools were used to predict the heat of formation and crystalline density of the 3,7-dinitro-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine molecule. Using this predicted data, we then ran Cheetah calculations to predict the performance of this novel material. Additionally, we predicted the qualitative impact sensitivity of this compound using electrostatic potential maps. This information has been transferred back to the requesting synthetic chemist, Dr David Chavez of Los Alamos National Laboratory.

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List of Symbols, Abbreviations, and Acronyms

6-31G*	Pople's Gaussian double-zeta polarized basis set with d polarization functions on each of the atoms Li through Ca
6-31G**	Pople's Gaussian double-zeta polarized basis set with d polarization functions on each of the atoms Li through Ca and p polarization functions on H and He
6-311++G(2df,2p)	Pople's Gaussian triple-zeta polarized basis set with $2d$ and f polarization functions on each of the atoms Li through Ca and $2p$ polarization functions on H and He along with s and p diffuse functions on each of the atoms Li through F and s diffuse functions on H and He
ν	balance parameter
Σ	average electrostatic surface potential
σ^2	variance of electrostatic surface potential
p	electronic density
$p_{crystal}$	crystalline density
$\Delta H^\circ_{f\,(g)}$	gas phase heat of formation
$\Delta H^\circ_{f\,(l)}$	liquid phase heat of formation
$\Delta H^\circ_{f\,(s)}$	solid phase heat of formation
V	electrostatic potential
ARL	US Army Research Laboratory
B3LYP	Becke 3 parameter exchange with Lee-Yang-Parr correlation DFT functional
DFT	density functional theory
ESP	electrostatic surface potential
g/cc	grams per cubic centimeter
kcal/mol	kilocalories per mole (unit of energy)
KS-DFT	Kohn-Sham density functional theory

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